that no anomalous shifts are induced by the halogens or by any of the 16 substituents singly or in combination at the 1,4 positions, suggesting perhaps that qualitative correlations of shift data with $\sigma$ constants provide little useful information concerning the nature of substituent effects.

Finally while qualitative agreement has been found between the internal shifts and the coupling constants for each family of disubstituted benzenes,[13] no strong correlations were noted. In general as the internal shift increases, the magnitudes of $J(2,3) = J(2',3')$ and $J(2,2') = J(3,3')$ increase; the largest internal shift and coupling values are found for the nitrobenzenes. In terms of trends the halogens influence abnormally large coupling values as does the *tert*-butyl group.

## Conclusions

We have seen that shift additivity relationships allow the accurate prediction of proton shifts in disubstituted benzenes. No inductive and/or resonance interactions between substituents have been noted despite the rather broad range of substitution examined. This study suggests the need for a fresh approach to the question of how aromatic substitution influences the shifts of ring protons. Group anisotropy effects do not explain the variations observed for different families of 1,4-disubstituted benzenes, nor can they account for the singlet proton resonances observed for compounds such as 4-iodonitrobenzene.

## Experimental Section

Spectral data were obtained on Varian A56/60, A60, and HA-100 spectrometers. Deuteriochloroform was the solvent for all families of 1,4-disubstituted benzenes except the benzoic acids. The latter were prepared in perdeuteriodimethyl sulfoxide. All spectra were analyzed by an IBM 360/50 computer using the program LAOCOON III.[18] The maximum permissible probable error was 0.03 Hz for the shift and coupling parameters. Standard least-squares programming was used to obtain the reported shift correlations.

Because of the scope of the investigation, a complete tabulation of synthetic procedures would be too voluminous. Commercially available compounds were purified before use by recrystallization or gas chromatography and authenticated by measurements of physical properties and by spectrophotometric identification procedures. Compounds not available from commercial sources were synthesized by standard techniques and verified by elemental analysis, measurements of physical properties, and spectrophotometric methods. Complete discussions are available on request.

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# Molecular Orbital Theory of the Hydrogen Bond. VII. A Series of Dimers Having Ammonia as the Proton Acceptor

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**Abstract:** *Ab initio* SCF calculations with a minimal STO-3G basis set have been performed on the series of dimers $ROH \cdots NH_3$, where R may be H, or one of the isoelectronic substituents $CH_3$, $NH_2$, OH, or F. The equilibrium structures and energies of these dimers are presented and analyzed. The dimer structures are well described in terms of the general hybridization model for the hydrogen bond. While the electrostatic interaction is of primary importance in stabilizing hydrogen bonded dimers, dipole–dipole and long-range interactions are also shown to be important in determining hydrogen bond strengths. Comparisons are made between corresponding dimers in the two series $ROH \cdots OH_2$ and $ROH \cdots NH_3$.

Within the past several years, *ab initio* molecular orbital theory has been applied to the problem of interacting molecules in studies of a rather wide variety of dimers in which the principal mode of intermolecular interaction is through hydrogen bond formation.[1-19] While the results of these studies may differ in certain specific details, collectively they have demonstrated that *ab initio* molecular orbital theory can be applied to the problem of hydrogen bond formation. Certainly, an ultimate aim of theoretical investigations of this type

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(1) K. Morokuma and L. Pedersen, *J. Chem. Phys.*, **48**, 3275 (1968).
(2) P. A. Kollman and L. C. Allen, *J. Chem. Phys.*, **51**, 3286 (1969).
(3) K. Morokuma and J. R. Winick, *J. Chem. Phys.*, **52**, 1301 (1970).
(4) G. H. F. Diercksen, *Chem. Phys. Lett.*, **4**, 373 (1969).
(5) G. H. F. Diercksen, *Theor. Chim. Acta*, **21**, 355 (1971).
(6) D. Hankins, J. W. Moskowitz, and F. H. Stillinger, *J. Chem. Phys.*, **53**, 4544 (1970).
(7) P. A. Kollman and L. C. Allen, *J. Chem. Phys.*, **52**, 5085 (1970).
(8) P. A. Kollman and L. C. Allen, *J. Amer. Chem. Soc.*, **93**, 4991 (1971).
(9) K. Morokuma, *J. Chem. Phys.*, **55**, 1236 (1971).
(10) L. Piela, *Chem. Phys. Lett.*, **15**, 199 (1972).
(11) A. Johansson, P. Kollman, and S. Rothenberg, *Chem. Phys. Lett.*, **16**, 123 (1972).
(12) A. Johansson, P. Kollman, and S. Rothenberg, *Theor. Chim. Acta*, **26**, 97 (1972).
(13) J. Del Bene and J. A. Pople, *J. Chem. Phys.*, **52**, 4858 (1970).
(14) J. E. Del Bene and J. A. Pople, *J. Chem. Phys.*, **55**, 2296 (1971).
(15) J. E. Del Bene, *J. Chem. Phys.*, **55**, 4633 (1971).
(16) J. E. Del Bene, *J. Chem. Phys.*, **56**, 4923 (1972).
(17) J. E. Del Bene, *J. Chem. Phys.*, **57**, 1899 (1972).
(18) J. E. Del Bene, *J. Chem. Phys.*, **58**, 3139 (1973).
(19) J. E. Del Bene and F. T. Marchese, *J. Chem. Phys.*, **58**, 926 (1973).

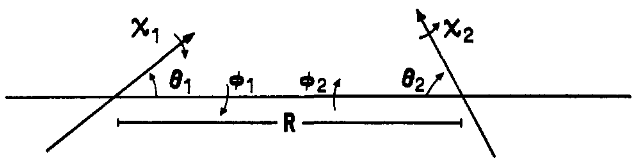

Figure 1. The intermolecular coordinate system. $\phi_1$ and $\phi_2$ are combined into the single parameter $\phi$ which has the same rotational sense as $\phi_2$. Curved arrows representing rotational senses pass in front of the lines they cross.

is to identify those factors which determine dimer structures and hydrogen bond energies. Of the many approaches which might be taken to fulfill this aim, the one which has been chosen in this and related studies is to examine systematically various series of dimers, using the same atomic orbital basis set. By following this approach, variations in calculated results due to a change in basis may be avoided.[20] Moreover, by examining a particular series of dimers and then comparing that series with others, trends in dimer structures and energies may become evident, and correlations may then be made. Papers I-III[15-17] reported the results of *ab initio* calculations on dimers formed from water and substituted water molecules, belonging to three series represented as ROH···$OH_2$, HOH···OHR, and $(ROH)_2$, where R may be H, or one of the isoelectronic substituents $CH_3$, $NH_2$, OH, or F. A study of the series of dimers having water or substituted water molecules as proton donors and formaldehyde as the proton acceptor, and represented as ROH···$OCH_2$, was next reported in paper IV.[18] In all series, the O-H···O hydrogen bond was investigated, and variations in dimer structures and O-H···O hydrogen bond energies were noted and analyzed. The following general statements concerning dimer structures and energies are supported by these studies.

(1) The structures of open chain dimers may be described in terms of a general hybridization model (GHM) for the hydrogen bond in which a directed lone pair of electrons on the proton acceptor molecule takes part in the formation of a linear or nearly linear hydrogen bond. The name of the model emphasizes the relationship between the hybridization (arrangement of bonds and lone pairs) of the proton acceptor atom and the direction in which the hydrogen bond forms.

(2) The primary factor responsible for stabilizing a hydrogen bonded dimer is the electrostatic interaction between the proton and the lone pair of electrons.

(3) Other factors which influence dimer structures and energies are the relative orientation of the permanent dipole moments of the proton donor and acceptor molecules and certain long-range interactions.

The study of the hydrogen bond has now been extended to include another series of dimers in which substituted water molecules act as proton donors to $NH_3$. This series contains O-H···N hydrogen bonds and may be represented by the formula ROH···$NH_3$, where R may vary as before. It is the purpose of this paper to report the structures and energies of these dimers, to analyze the dimer structures and energies in terms of those factors previously found to be of importance in determining dimer structures and energies, and to compare these dimers with the dimers ROH···$OH_2$ in which $H_2O$ rather than $NH_3$ is the proton acceptor molecule.

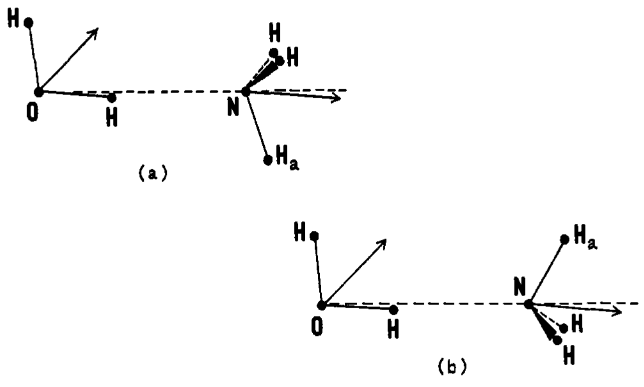

Figure 2. The dimers HOH···$NH_3$ showing the principal axes: (a) dimer with $\chi_2 = 0°$; (b) dimer with $\chi_2 = 60°$.

## Method of Calculation

The closed shell ground states of monomers and dimers may be described by single determinant wave functions composed of sets of molecular orbitals (MO's), each occupied by a pair of electrons. Each MO $\psi_i$ is approximated as a linear combination of atomic orbitals $\phi_\mu$ (the LCAO approximation)

$$\psi_i = \sum_{\mu} c_{\mu i} \phi_\mu$$

where the expansion coefficients $c_{\mu i}$ are determined in the usual manner by solving the Roothaan equations.[21] In this work, as in the studies reported in papers I-VI[15-19,22] of this series, the STO-3G basis set with standard scale factors has been used for the LCAO expansion.[23]

The geometries of the proton donors and the proton acceptor $NH_3$ molecule are optimized STO-3G geometries which are held rigid for all dimer calculations.[15-17,24] In order to describe the structures of the dimers, it is necessary to define intermolecular coordinates consisting of an intermolecular distance ($R$) and a set of intermolecular angles, as shown in Figure 1. For the dimers ROH···$NH_3$, the intermolecular distance ($R$) is the O-N distance measured along the intermolecular line. The intermolecular angles measure rotations with respect to principal axes, which must also be selected in the monomers. For $H_2O$, the obvious choice for a principal axis is the $C_2$ symmetry axis. For a substituted water molecule which has no symmetry axis in the X-O-H plane (X is the nonhydrogen atom of the R group), the principal axis is most conveniently chosen as the bisector of the X-O-H angle. The $C_3$ symmetry axis in $NH_3$ is the principal axis in the proton acceptor molecule. In the starting orientation from which the coordinates of the proton donor and proton acceptor molecules are generated, the molecules are placed in the intermolecular coordinate system such that their principal axes point inward along the intermolecular line (see Figures 1 and 2). The angle $\theta_1$ is then the angle between the principal axis of

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(20) J. E. Del Bene and J. A. Pople, *J. Chem. Phys.*, 58, 3605 (1973).

(21) C. C. J. Roothaan, *Rev. Mod. Phys.*, 23, 69 (1951).

(22) J. E. Del Bene, *J. Amer. Chem. Soc.*, submitted for publication.

(23) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, 51, 2657 (1969).

(24) M. D. Newton, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, 52, 4064 (1970).

the proton donor and the intermolecular line, while $\chi_1$ measures rotation of the proton donor molecule about its own principal axis. The angles $\theta_2$ and $\chi_2$ measure similar rotations in the proton acceptor molecule. $\phi_1$ and $\phi_2$ are combined into the single angle $\phi$, which measures rotation of the principal axis of the proton acceptor molecule about the intermolecular line, and which has the same rotational sense as $\phi_2$. For convenience, the angle $\theta_1'$ is defined as

$$\theta_1' = \theta_1 - \angle_{\text{X-O-H}}/2$$

Defined in this way, $\theta_1'$ measures the angle between the O-H bond of the proton donor molecule and the intermolecular O-N line. Its magnitude and sign directly indicate any deviation from linearity ($\theta_1' = 0°$) of the O-H···N bond.

## Results and Discussion

*Ab initio* SCF calculations with the minimal STO-3G basis set have been performed to determine the structures and hydrogen bond energies of the dimers ROH···$NH_3$. All calculations were performed in double precision on an IBM 360/50 computer until a minimum energy structure was obtained for each dimer with respect to a ±0.01 Å change in $R$ and ±1° in each of the intermolecular angles, where such refinement was possible (see discussion below). The intermolecular energy (hydrogen bond energy) is computed, at that point on the intermolecular potential surface at which the optimized intermolecular coordinates are found, by subtracting the sum of the energies of ROH and $NH_3$ from the energy computed for ROH···$NH_3$. The optimized intermolecular coordinates and the hydrogen bond energies for the dimers ROH···$NH_3$ are reported in Table I.

**Table I.** Dimer Structures and Energies[a]

| ROH···$NH_3$ R = | $R$, Å | $\theta_1'$, deg | $\chi_1$, deg | $\theta_2$, deg | $\chi_2$, deg | $\phi$, deg | $\Delta E$, au[b] |
|---|---|---|---|---|---|---|---|
| H | 2.91 | −3 | 0 | 176 | 0 | 180 | −0.00939 |
|  | 2.91 | −3 | 0 | 176 | 60 | 180 | −0.00939 |
| $CH_3$ | 2.87 | −2 | 0 | 177 | 0 | 180 | −0.01032 |
|  | 2.87 | −2 | 0 | 177 | 60 | 180 | −0.01031 |
| $NH_2$ | 2.81 | −3 | 0 | 172 | 0 | 0 | −0.01129 |
|  | (2.81)[c] | (−3) | (0) | (173) | (60) | (0) | (−0.01122) |
| OH | 2.80 | −2 | 0 | 176 | 9 | 21 | −0.01276 |
| F | 2.77 | −1 | 0 | 179 | 0 | 0 | −0.01562 |
|  | 2.77 | −1 | 0 | 179 | 60 | 0 | −0.01562 |

[a] See text for a discussion of the double entries. [b] $\Delta E$ is the hydrogen bond energy. 1 au = 627.49 kcal/mol. [c] Dimer with $\chi_2 = 60°$ is not an equilibrium structure.

**Dimer Energies and Distances.** As seen in Table I, the hydrogen bond strength in the dimers ROH···$NH_3$ increases as R varies from H to $CH_3$, $NH_2$, OH, and F. Hence, the order of increasing hydrogen bond strength follows the order of increasing $\sigma$ electron withdrawing ability of the substituent R in the ROH molecule. This same type of correlation was observed previously in other series of dimers and has been interpreted as demonstrating the prime importance of the electrostatic interaction in stabilizing hydrogen bonded dimers.[17,18] Another correlation which is once again evident from the data of Table I occurs between the intermolecular distance and the hydrogen bond strength. In the dimers ROH···$NH_3$, the intermolecular distance decreases as the strength of the hydrogen bond increases.

**Table II.** Mulliken Gross Atomic Populations for Monomers and Dimers[a]

|  | X[b] | O | H | N | $H_a$[c] | $H_b$ |
|---|---|---|---|---|---|---|
| $NH_3$ |  |  |  | 7.474 | 0.842 | 0.842 |
| $H_2O$ | 0.835 | 8.330 | 0.835 |  |  |  |
| $H_2O$-$NH_3$ | 0.865 | 8.380 | 0.795 | 7.481 | 0.825 | 0.828 |
| $CH_3OH$ | 6.071 | 8.280 | 0.826 |  |  |  |
| $CH_3OH$-$NH_3$ | 6.072 | 8.330 | 0.780 | 7.480 | 0.824 | 0.825 |
| $NH_2OH$ | 7.279 | 8.223 | 0.805 |  |  |  |
| $NH_2OH$-$NH_3$ | 7.292 | 8.278 | 0.758 | 7.479 | 0.818 | 0.824 |
| $H_2O_2$ | 8.189 | 8.189 | 0.811 |  |  |  |
| $H_2O_2$-$NH_3$ | 8.213 | 8.249 | 0.762 | 7.480 | 0.819 | 0.822[d] |
| HOF | 9.048 | 8.148 | 0.804 |  |  |  |
| HOF-$NH_3$ | 9.089 | 8.219 | 0.757 | 7.483 | 0.817 | 0.817 |

[a] Data in this table refer specifically to the first entry in Table I for each dimer. [b] For $H_2O$, X = H. For substituted water molecules, X is the nonhydrogen atom of the R group. [c] For dimers with $C_s$ symmetry, $H_a$ lies in the symmetry plane. [d] In $H_2O_2$-$NH_3$, there is no symmetry equivalence of $NH_3$ protons. Population of $H_c$ is 0.821.

**Dimer Structures.** As noted above, dimer structures may be described in terms of the general hybridization model for the hydrogen bond. The model is based on two features of the hydrogen bond which have important structural consequences, namely, the *directed lone pair of electrons* and the *linear X-H··· Y bond.* On the basis of the general hybridization model, the dimers ROH···$NH_3$ should then be expected to have optimized structures in which $\theta_2 = 180°$ (to provide the directed lone pair) and $\chi_1 = \theta_1' = 0°$ (for the linear O-H···N bond). The equilibrium dimer structures as described in Table I agree quite well with the structures expected from GHM. In particular, the optimized values of $\chi_1$ and $\theta_1'$ indicate that the hydrogen bonds in these dimers deviate from linearity by at most 3°. Values of $\theta_2$ range from 176 to 179° in four of the dimers, with a somewhat smaller value of 172° occurring in $NH_2OH$-$NH_3$. In the dimers $NH_2OH$-$H_2O$ and $NH_2OH$-$H_2CO$ with $NH_2OH$ as the proton donor, it was also observed that the optimized values of $\theta_2$ were somewhat less than anticipated from GHM. In addition, rather large deviations of the O-H···O bonds from linearity were found in these dimers.[17,18] As a result of these structural changes, the distance between the $NH_2OH$ nitrogen atom and the hydrogens of $H_2O$ and $H_2CO$ decreased. Hence it was suggested that such deviations from expected dimer structures were produced by certain favorable long-range N-H interactions. In $NH_2OH$-$NH_3$, the equilibrium dimer structure (with $\chi_2 = 0°$) does allow the $NH_3$ hydrogen, which lies in the plane defined by the principal axis of the proton donor and the intermolecular line, to approach the nitrogen atom of $NH_2OH$ as $\theta_2$ becomes less than 180°. In this dimer, the difference in the charges on this proton and the others (labeled $H_b$ in Table II) is at a maximum in the series. These observations suggest that a long-range N-H interaction might also be responsible for the somewhat larger deviation of the angle $\theta_2$ from 180° in this dimer. However, it should be noted that the O-H···N bond in this dimer does not show an increased deviation from linearity (which would enhance this interaction) when compared with the other dimers in this series. Moreover, in this dimer, the $NH_3$ molecule is still essentially free to rotate about its $C_3$ axis (see discussion below). It would therefore appear that the long-range N–H interaction in this dimer is a very weak one, even in a relative sense when compared with the favorable N–H interactions in the dimers $NH_2OH$–$H_2O$ and $NH_2OH$–$H_2CO$ in which $NH_2OH$ is also the proton donor.

As seen in Table I, for all dimers except $H_2O_2$–$NH_3$ two structures are reported. It is appropriate to now comment on the structures described by each entry. It should be noted that each dimer in the series $ROH\cdots NH_3$ except $H_2O_2$–$NH_3$ possesses a symmetry plane defined by the principal axis of the proton donor molecule and the intermolecular line and preserved by values of $\chi_1 = 0°$, $\chi_2 = 0$ or $60°$, and $\phi = 0$ or $180°$. If the first and second entries in Table I for each dimer are compared, it is observed that these two structures can be readily differentiated by their $\chi_2$ values. For the dimers having $C_s$ symmetry, both structures were optimized with respect to all coordinates except $\chi_2$ (which is fixed by symmetry at either 0 or 60°). For the dimer $NH_2OH$–$NH_3$, the structure having $\chi_2 = 60°$ is not an equilibrium structure on the intermolecular potential surface with respect to variation of this coordinate. Its energy is $7 \times 10^{-5}$ au higher than that of the equilibrium dimer with $\chi_2 = 0°$. For the other $C_s$ dimers, the optimized intermolecular coordinates for the $\chi_2 = 0°$ and $\chi_2 = 60°$ structures are identical, and the energy difference between the two structures is no more than $1 \times 10^{-5}$ au, with a flat potential curve connecting the two forms. Since $\chi_2$ measures rotation of the $NH_3$ molecule about its own $C_3$ axis, $\chi_2$ values of 0 and 60° correspond to two particular conformations in the dimers in which the $NH_3$ N–H bonds eclipse or stagger the O–X bond in the proton donor molecule, as illustrated for $H_2O$–$NH_3$ in Figure 2. The calculated results indicate that for $H_2O$–$NH_3$, $CH_3OH$–$NH_3$, and $HOF$–$NH_3$ neither conformation is preferred, and no rotational barrier exists between the two forms. In $NH_2OH$–$NH_3$, the eclipsed conformation (with $\chi_2 = 0°$) is preferred, but even in this case the barrier to free rotation is less than $1 \times 10^{-4}$ au (0.06 kcal/mol). In $H_2O_2$–$NH_3$, which has no symmetry plane, the rotational barrier is 0.02 kcal/mol. Therefore, it appears that there is essentially free rotation of the $NH_3$ molecule about its own $C_3$ axis in all dimers $ROH\cdots NH_3$.[25]

A factor which has previously been shown to influence the structures of hydrogen bonded dimers is the relative orientation of the permanent dipole moments of the proton donor and proton acceptor molecules. For open-chain dimers $ROH\cdots OH_2$, $HOH\cdots OHR$, $(ROH)_2$, and $ROH\cdots OCH_2$, it was observed that the structure which was necessary to provide for the directed lone pair of electrons precluded a head-to-tail alignment of the permanent dipole moments of the proton donor and acceptor molecules. Rather in these dimers, the relative orientation of the dipoles could vary from a parallel to somewhat antiparallel alignment as the $\phi$ coordinate varied, while still leaving the hydrogen bond essentially intact. It was generally observed that the optimized value of the $\phi$ coordinate was one which allowed the dipole moments to approach a somewhat antiparallel alignment.[16–18] To assess the importance of the relative orientation of the permanent dipole moments of the proton donor and proton acceptor molecules in determining the structures of dimers $ROH\cdots NH_3$, it is necessary only to recognize that the lone pair and the dipole moment of $NH_3$ both lie along its $C_3$ symmetry axis. Since the lone pair of electrons must be directed along the intermolecular line for hydrogen bond formation, the dipole moment of $NH_3$ must also lie along this line. Therefore, changes in dimer structures associated with changes in the $\phi$ coordinate will have little effect on the relative orientation of the permanent dipole moments of ROH and $NH_3$. Hence, the alignment of the dipoles would not be expected to influence the structures of dimers $ROH\cdots NH_3$ to any significant extent.[26]

Although the structures of the dimers $ROH\cdots NH_3$ can be quite well described by the general hybridization model for the hydrogen bond, the equilibrium dimer structures are seen to deviate to a slight extent from the idealized structures provided by GHM. While these slight deviations are interesting in themselves, it is important to realize that they by no means limit the predictive value of GHM, nor are the deviations of sufficient magnitude to cast doubt on the concepts on which the model is based. This may be substantiated by comparing the energies of the equilibrium dimers with the energies of dimers having the idealized structures suggested by GHM. To make this comparison, a calculation was carried out for each dimer in the series in which the intermolecular distance was fixed at the optimized distance reported in Table I and in which $\theta_1' = \chi_1 = 0°$ and $\theta_2 = 180°$. The hydrogen bond energies of the resulting dimers were found to be within 0.1 kcal/mol of the energies of the equilibrium dimers. This comparison implies that normal thermal motion would produce distortions of the dimer structures which are larger than the deviations from idealized structures computed in this work.

**Population Analysis and Force Constants.** It is of interest to examine atomic populations and force constants for the dimers $ROH\cdots NH_3$. The Mulliken gross atomic populations[27] for the appropriate monomers and dimers are given in Table II. The population changes which occur upon dimer formation in this series are typical of changes which have been previously observed. Dimer formation is accompanied by a small amount of charge transfer from the proton acceptor $NH_3$ molecule to the proton donor. The amount of charge transfer varies from 0.04 electron in $H_2O$–$NH_3$ and increases in the series to 0.07 electron in $HOF$–$NH_3$. Despite the loss of electron density by $NH_3$, the $NH_3$ nitrogen atom is slightly more negatively charged in the dimer than it is in the monomer. Hence, electron transfer from $NH_3$ occurs at the expense of the $NH_3$ protons. As a result, the $NH_3$ molecule in the dimer would tend to be a stronger proton donor than $NH_3$ itself. Obviously, the electron density of the proton donor molecule must then increase upon dimer formation. This increase is observed primarily as an increase

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(25) It is important to recognize that this level of theory can account for rotational barriers in molecules. Thus, *ab initio* SCF calculations with the STO-3G basis set and the rigid rotor model predict a rotational barrier of 3.33 kcal/mol for ethane, in reasonable agreement with the experimental value of 2.93 kcal/mol: see L. Radom and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 4786 (1970).

(26) Note that at $\theta_2 = 180°$, the $\phi$ rotation is no longer even defined.

(27) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).

in the electron density of the hydroxyl oxygen, since the hydrogen bonded proton loses electron density upon dimer formation. Hence, the oxygen of the proton donor molecule would tend to be a better proton acceptor in the dimer than it is in an isolated monomer. The tendency for the hydroxyl oxygen of the proton donor molecule to become more negatively charged while the protons in the proton acceptor molecule become more positively charged upon dimer formation is a general one, which has been related to the nonadditivity of hydrogen bond energies in larger polymers having chain type structures.[13-15]

Some estimates of the rigidity of dimer structures may be obtained by calculating the second derivatives of the dimer energies with respect to the intermolecular coordinates. These derivatives are approximated by changing each angle by ±20° and the intermolecular distance by ±0.1 Å and using the formula

$$\partial^2\epsilon/\partial x^2 \approx [\epsilon(x + \Delta) + \epsilon(x - \Delta) - 2\epsilon(x)]/\Delta^2$$

where $\epsilon$ is the intermolecular energy, $x$ is the optimized value of the coordinate, and $\Delta$ is the change in the coordinate. The derivatives with respect to $R$, $\theta_1$, $\chi_1$, and $\theta_2$ for the dimers $ROH\cdots NH_3$ are given in Table III.

**Table III.** Second Derivatives of Intermolecular Energies[a-c]

| | $\partial^2\epsilon/\partial x^2$, $x$ = | | | |
|---|---|---|---|---|
| | $R$ | $\theta_1$ | $\chi_1$ | $\theta_2$ |
| $H_2O-NH_3$ | 0.01829 | 0.03766 | 0.02457 | 0.02005 |
| $CH_3OH-NH_3$ | 0.01969 | 0.05293 | 0.03152 | 0.02240 |
| $NH_2OH-NH_3$ | 0.02369 | 0.06982 | 0.03997 | 0.02505 |
| $H_2O_2-NH_3$ | 0.02610 | 0.06359 | 0.04166 | 0.01939 |
| $HOF-NH_3$ | 0.03041 | 0.06689 | 0.04739 | 0.03111 |

[a] In atomic units with angles in radians. [b] No derivatives with respect to $\chi_2$ and $\phi$ are reported, since rotations measured by these two angles are essentially free. [c] See footnote *a* of Table II.

No derivatives with respect to $\chi_2$ and $\phi$ have been reported since rotations measured by these two angles are essentially free. With respect to each intermolecular coordinate, the force constants generally increase as the hydrogen bond strength increases. Exceptions to this occur in the $\theta_1$ derivative of $NH_2OH-NH_3$ (perhaps due to the N-H long-range interaction) and in $H_2O_2-NH_3$ (where 20° changes in $\theta_2$ do not have the same effect as in other dimers with $C_s$ symmetry). With respect to angular distortions of the dimer structures, it can be seen that rotation of the proton donor molecule is quite difficult, since such a rotation severely weakens the hydrogen bond by removing the proton. On the other hand, distortions of the dimer structure which turn the lone pair away from the intermolecular line (the $\theta_2$ motion) are not quite as energetically unfavorable.

**$H_2O$ *vs.* $NH_3$ as a Proton Acceptor.** Interesting comparisons can be made between the two series of dimers $ROH\cdots NH_3$ and $ROH\cdots OH_2$. Statements that $NH_3$ is a stronger base than $H_2O$ abound in the literature, and there is a tendency to interpret such statements as indicating that hydrogen bonds formed with $NH_3$ as the proton acceptor will be stronger than those formed with $H_2O$, providing that the proton donor molecule is the same in both cases. In so far as the electrostatic interaction is of primary importance in determining base strength and hydrogen bond strength, a correlation between these two properties might well be anticipated. However, the interaction of the permanent dipoles and long-range interactions are additional factors which have been shown to influence dimer structures. A pairwise comparison of corresponding dimers from the two series $ROH\cdots NH_3$ and $ROH\cdots OH_2$ will demonstrate that such secondary factors are also important in determining relative hydrogen bond strengths.

A comparison of the hydrogen bond energies of the first two members of these series (see Table IV) shows that the hydrogen bond in the dimer $HOH\cdots NH_3$ is predicted to be slightly stronger than that in $HOH\cdots OH_2$, although the calculated energy difference is rather insignificant (0.01 kcal/mol). Other calculations on these two dimers employing basis sets which give monomer energies closer to the Hartree–Fock limit also predict that the hydrogen bond in $HOH\cdots NH_3$ is stronger than that in $HOH\cdots OH_2$. However, even with such large basis sets, the predicted difference in hydrogen bond strengths is still only 0.5 kcal/mol.[8] From an electrostatic point of view, the larger negative charge on nitrogen in $NH_3$ would tend to favor it as a proton acceptor over the oxygen of $H_2O$ (see Table II). However, due to the lower nuclear charge on the nitrogen atom, the orbital containing the lone pair of electrons on nitrogen is more diffuse than the corresponding oxygen orbital, and the radial extent of the nitrogen lone pair is greater. As a result, intermolecular oxygen–nitrogen distances in $O-H\cdots N$ bonds tend to be longer than oxygen–oxygen distances in $O-H\cdots O$ bonds, as seen in Table IV. This difference in intermolecular distances might also influence the relative stabilities of $O-H\cdots O$ and $O-H\cdots N$ hydrogen bonds.[28]

**Table IV.** Intermolecular Energies and Distances in Dimers $ROH\cdots NH_3$ and $ROH\cdots OH_2$[a]

| | Proton acceptor | | | |
|---|---|---|---|---|
| | $NH_3$ | | $H_2O$ | |
| Proton donor | $R$, Å | $\Delta E$, kcal/mol | $R$, Å | $\Delta E$, kcal/mol |
| $H_2O$ | 2.91 | 5.89 | 2.74 | 5.88 |
| $CH_3OH$ | 2.87 | 6.48 | 2.71 | 6.26 |
| $NH_2OH$ | 2.81 | 7.08 | 2.66 | 7.30 |
| $H_2O_2$ | 2.80 | 8.01 | 2.67 | 7.64 |
| HOF | 2.77 | 9.80 | 2.65 | 8.72 |

[a] Data for dimers $ROH\cdots OH_2$ taken from ref 17.

The second members of the two series of dimers have $CH_3OH$ as the proton donor molecule. The dimer in which $NH_3$ is the proton acceptor is once again predicted to be more stable than the dimer having $H_2O$ as the proton acceptor molecule. The difference in the stabilities of the two dimers is more significant here, amounting to 0.22 kcal/mol. The difference in the stabilities of the dimers $NH_2OH-NH_3$ and $NH_2OH-H_2O$ is also 0.22 kcal/mol, but now the dimer formed with $H_2O$ as the proton acceptor is more stable. This "reversal" of order may be explained by noting that the structure of the dimer $NH_2OH-H_2O$ is influenced by a favorable long-range N-H interaction. This long-range

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(28) Note that within either series of dimers, intermolecular distances decrease as hydrogen bond strengths increase. However, intermolecular $O-H\cdots N$ distances are longer than $O-H\cdots O$ distances, independent of the relative stabilities of the hydrogen bonds.

N–H interaction is apparently much stronger than a similar interaction in $NH_2OH–NH_3$. Thus, in $NH_2OH–H_2O$, the N–H interaction not only compensates for the expected decrease in hydrogen bond strength due to the less than optimum orientation of the acceptor $H_2O$ molecule and the nonlinear O–H···O bond, but it is sufficiently strong to stabilize this dimer to the extent that it is more stable than $NH_2OH–NH_3$. Hence, a secondary interaction identified originally from structural changes in dimers must now be invoked to explain a reversal of the relative energies of the corresponding dimers $NH_2OH–H_2O$ and $NH_2OH–NH_3$.

The dimers $H_2O_2–NH_3$ and $HOF–NH_3$ are predicted to be more stable than $H_2O_2–H_2O$ and $HOF–H_2O$, respectively. However, whereas the difference in stabilities of the dimers having $H_2O_2$ as the proton donor is 0.37 kcal/mol, the dimer $HOF–NH_3$ is significantly more stable than $HOF–H_2O$ by 1.08 kcal/mol. The enhanced stability of $HOF–NH_3$ may be explained by another of the secondary factors previously identified as influencing dimer structures, namely, the relative orientation of the permanent dipole moments of the proton donor and acceptor molecules. As noted previously, in the molecule HOF the dipole moment vector makes an angle of less than 1° with the O–H bond.[17] Hence, when HOF is the proton donor, the angle between the dipole moment vector of HOF and the intermolecular line will also be quite small. As noted above, when $NH_3$ is the proton acceptor molecule, the requirement for the directed lone pair for hydrogen bond formation also places the dipole moment of $NH_3$ along the intermolecular line. Hence, in the dimer $HOF–NH_3$ there exists a favorable alignment of permanent dipole moments, and this interaction gives additional stability to this dimer. Such an alignment is not possible in $HOF–H_2O$.

While it has been possible to correlate the charge on the proton acceptor atom with the strength of the hydrogen bond within a given series of dimers, the preceding comparisons suggest that simple correlations between charges on nitrogen and oxygen and relative strengths of O–H···O and O–H···N hydrogen bonds may not always exist. While the electrostatic interaction may be the primary factor responsible for stabilizing a hydrogen bonded dimer, the lack of complete correlation between atomic charges and hydrogen bond strengths demonstrates that additional factors also influence hydrogen bond energies. It is not surprising then to find that the relative stabilities of two corresponding dimers $ROH–NH_3$ and $ROH–H_2O$ reflect a dependence on the proton donor ROH molecule.

An interesting comparison can also be made between the $R$ and $\theta_2$ derivatives for corresponding dimers in the two series $ROH\cdots NH_3$ and $ROH\cdots OH_2$. The dimer $ROH\cdots NH_3$ is always less rigid than the corresponding dimer $ROH\cdots OH_2$ with respect to changes in the intermolecular distance. That the potential curve with respect to changes in the intermolecular distance is more broad in the dimer having $NH_3$ as the proton acceptor is consistent with the greater radial extent of the nitrogen lone pair and the longer intermolecular O–N distance. On the other hand, angular distortions of the dimer structures which bend the proton acceptor lone pair away from the intermolecular line are easier in $ROH\cdots OH_2$ than in the corresponding dimer $ROH\cdots NH_3$. The relative ease with which the $H_2O$ molecule may be rotated can be attributed to the existence of a double minimum in the potential curve for the intermolecular energy as a function of $\theta_2$ in dimers $ROH\cdots OH_2$. The double minimum is associated with the formation of hydrogen bonds through each of the lone pairs of electrons on oxygen. Of course, the potential curve for variation of $\theta_2$ in a dimer $ROH\cdots NH_3$ has only a single minimum near $\theta_2 = 180°$.

## Conclusions

(1) Within the series of dimers $ROH\cdots NH_3$, the order of increasing hydrogen bond strength follows the order of increasing $\sigma$ electron withdrawing ability of the substituent R. This type of correlation, which has also been observed in other series of dimers, suggests that the electrostatic interaction is of primary importance in determining the strength of a hydrogen bond.

(2) The structures of the dimers $ROH\cdots NH_3$ can be described by the general hybridization model for the hydrogen bond, in which a directed lone pair of electrons on the proton acceptor atom takes part in the formation of a linear, or nearly linear, hydrogen bond. In these dimers, there is essentially free rotation of the $NH_3$ molecule about its own $C_3$ axis, as this rotation leaves the hydrogen bond intact.

(3) Hydrogen bond formation is accompanied by a small amount of charge transfer from $NH_3$ to the proton donor ROH molecule. In dimers $ROH\cdots NH_3$, the hydroxyl oxygen acquires a larger negative charge, while the hydrogen bonded proton and the $NH_3$ protons become more positively charged in the dimer than they are in the monomers.

(4) The relative stabilities of corresponding dimers from the two series $ROH\cdots NH_3$ and $ROH\cdots OH_2$ reflect a dependence on the specific nature of the proton donor ROH molecule. This suggests that factors other than the electrostatic interaction also contribute to the stabilization of hydrogen bonded dimers. Among these factors are dipole–dipole and long-range interactions in the dimers and the radial extent of the lone pairs on the proton acceptor atoms.

(5) Distortions of dimer structures introduced through changes in the intermolecular distance are always easier in $ROH\cdots NH_3$ than in the corresponding dimer $ROH\cdots OH_2$, independent of the relative hydrogen bond strengths. However, distortions associated with bending the directed lone pair of electrons on the proton acceptor atom away from the intermolecular line are always more difficult in $ROH\cdots NH_3$ than in the corresponding dimer $ROH\cdots OH_2$.

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